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Wastes from Manufacture of Dyes and Pigments. Volume 6. Methine and Polymethine Dyes and Pigments

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WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOLUME 6. METHINE AND POLYMETHINE DYES AND PIGMENTS

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A preliminary study of the manufacture of methine and polymethine dyes and pigments was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced, and the known U.S. producers. The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and four companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a series of preliminary studies of segments of the dye and pigment manufacturing industry conducted for the Organic and Inorganic Chemicals and Products Branch of the Industrial Pollution Control Division. The objective of these studies was to determine if process waste streams might contain hazardous material and to recommend sites where a sampling program could be used to confirm the nature of any hazards that were identified.

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ABSTRACT

A preliminary study of the manufacture of methine and polymethine dyes and pigments was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced, and the known U.S. producers. The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and four companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

This report is submitted in fulfillment of Contract No. 68-03-2944 by SRI International under the sponsonship of the U.S. Environmental Protection Agency. The report covers the period December 1981 to August 1982, and work was completed as of July 31, 1983.

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SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed of in a manner that limits the release of hazardous materials to the environment. To date, many specific waste streams from manufacturing processes are listed in regulations as being hazardous because of their chemical composition. The objective of this preliminary study is to determine if wastes produced by the manufacture of dyes and pigments in the United States might require listing as hazardous materials. An analysis of both the chemistry and the physical processing involved in dye and pigment manufacturing is used to identify all wastes that may contain significant chemical hazards. An analysis of the industry is used to determine specific manufacturers where the candidate wastes may be produced. This information allows contractors of the U.S. Environmental Protection Agency to design a sampling and analysis program to confirm or disprove the presence of hazardous materials in the candidate wastes and thereby develop a basis for listing dye and pigment manufacturing wastes under RCRA. This report deals with the wastes from the manufacture of methine and polymethine dyes and pigments.

In 1972, production of 2,500 metric tons for all methine and polymethine dyes was reported to the U.S. Tariff Commission (1974). This represents 2% of the total reported U.S. dye production of 120,000 metric tons for that year. Methine and polymethine dyes (and pigments) represented the fifth largest structural class of dyes based on U.S. production volume. Data on U.S. production by structural class has not been reported since 1972, so it is not possible to determine from public sources whether the relative importance or total production of methine and polymethine dyes and pigments has changed.

Table 1 gives 1979 U.S. production data for the 33 commercially significant methine and polymethine dyes and pigments, that is, dyes produced at greater than 2.3 metric tons and pigments produced at greater than 0.5 metric tons. These 1979 U.S. production levels are from the Organic Dyes and Pigments Data Base, prepared by SRI International for the EPA (Swett et al., 1983). For 23 dyes and 2 pigments the production is shown only as an amount greater than a minimum number. These are dyes and pigments produced by fewer than three manufacturers or by three or more where one or two dominate the market. Public sources do not list specific production amounts in these cases. Production data are for the commercial product, which may include solvents, other diluents, and impurities in addition to the specific dye chemical of interest; concentration of the organic dye in the commercial product may vary from 10% to 100%. No specific information was available

Table 1

METHINE AND POLYMETHINE DYES AND PIGMENTS INCLUDED IN THIS STUDY

C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)
48013	Basic Violet 16	120
48020	Basic Violet 7	> 2.3
48035	Basic Orange 21	227
48054	Basic Yellow 28	> 4.5
48055	Basic Yellow 11	249
48070	Basic Red 12	> 6.8
48100	Basic Yellow 23	> 2.3
48420	Disperse Yellow 99	> 2.3
--	Basic Blue 69	> 2.3
--	Basic Red 14	186
--	Basic Red 15	92
--	Basic Red 49	53
--	Basic Violet 15	> 2.3
--	Basic Yellow 13	81
--	Basic Yellow 21	> 2.3
--	Basic Yellow 29	288
--	Basic Yellow 49	> 2.3
--	Basic Yellow 53	> 2.3
--	Basic Yellow 58	> 2.3
--	Basic Yellow 64	> 2.3
--	Basic Yellow 65	> 2.3
--	Basic Yellow 78	> 2.3
--	Basic Yellow 79	> 2.3
--	Disperse Yellow 88	> 2.3
--	Disperse Yellow 93	> 2.3
--	Disperse Yellow 118	> 2.3
--	Disperse Yellow 125	> 2.3

Table 1 **(Concluded)**

C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)
--	Disperse Yellow 131	> 2.3
--	Disperse Yellow 200	> 2.3
--	Disperse Yellow 207	> 2.3
--	Disperse Yellow 208	> 2.3
--	Pigment Yellow 129	> 0.5
--	Pigment Yellow 139	> 0.5

concerning the concentration of the dye in the commercial product. Table 1 is arranged according to the Colour Index (C.I.) number (Colour Index, The Society of Dyers and Colourists, 1980).

Eight of the 33 dyes and pigments listed in Table 1 have a known 1979 U.S. commercial production volume. These dyes are listed in Table 2, arranged according to their production volume. These eight dyes represent a combined 1979 U.S. commercial production of 1,296 metric tons. Each of these dyes is produced by at least three manufacturers.

Usually several manufacturers are required to produce a dye in large volume, because of the relative small batch production operations of the dye and pigment industry (Steadman et al., 1977). Of the remaining 25 dyes and pigments with unknown commercial production in 1979, all but two were produced by only one manufacturer and therefore probably produced in relatively small amounts. The two exceptions were C.I. Basic Yellow 28 (C.I. 48054) and C.I. Basic Red 12 (C.I. 48070). In 1978, C.I. Basic Yellow 28 was produced in the United States by four manufacturers with a total combined production of 325 metric tons. In 1979, only two manufacturers were still producing it; however, there is reason to suspect it was produced in significant amounts. In 1979, three manufacturers were producing C.I. Basic Red 12, but the total production was not reported. No production information was available for 1978; however, in 1980, three manufacturers produced C.I. Basic Red 12 for a total combined commercial production of 49 metric tons. Therefore it is reasonable to believe that these two dyes were produced in significant quantities in 1979.

Eight dyes listed in Table 1 with a Colour Index number have a known chemical structure and the process chemistry is known for seven of them. However, only three of these dyes have known 1979 U.S. commercial production, listed in Table 2. In the following sections of this report, the process chemistry of the methine and polymethine dyes and pigments and sources of wastes during dye and pigment manufacture are discussed in detail.

Table 2

METHINE AND POLYMETHINE DYES AND PIGMENTS
OF KNOWN 1979 U.S. COMMERCIAL PRODUCTION

C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)
--	Basic Yellow 29	288
48055	Basic Yellow 11	249
48035	Basic Orange 21	227
--	Basic Red 14	186
48013	Basic Violet 16	120
--	Basic Red 15	92
--	Basic Yellow 13	81
--	Basic Red 49	53

SECTION 2

SUMMARY AND CONCLUSIONS

In this preliminary study of methine and polymethine dyes and pigments, several waste streams were identified that might contain hazardous materials:

- Discarded shipping containers. These would contain dye and pigment intermediates.
- Wastewater treatment solids. The evidence indicates that the solids will be contaminated with low levels of all of the dye and pigment intermediates as well as the dyes and pigments themselves and some reaction by-products.
- Process wastewater that may contain the mother liquor from filtering operations. This is probably the major source of discharge of organic chemicals from most plants.

The information on the producers of dyes and pigments contained in Section 5 (Tables 7 and 9) along with the production volume information of Table 2 was analyzed to choose a few representative manufacturers where a sampling program might be conducted to determine the composition of the waste emissions. The following companies are recommended:

Atlantic Chemical Corp.

Mobay Chemical Corp.

BASF Wyandotte Corp.

Toms River Chemical Corp.

The four companies that are recommended for a sampling program should yield samples from facilities using different manufacturing and waste treatment practices. Because there is considerable overlap in the actual dyes they produce, the four-company sampling program increases the chances of identifying material in the waste streams from manufacturing the same dye or pigment that may be sensitive to plant practices.

SECTION 3

PROCESS CHEMISTRY

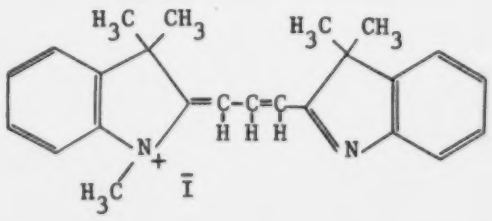
INTRODUCTION

A discussion of the production of methine and polymethine dyes and pigments is necessary to identify the emission sources and wastes that might be hazardous. This section focuses on the chemistry of the dye and pigment synthesis, with special attention given to the starting materials, intermediates, reaction conditions, and potential byproducts.

The methine and polymethine dyes and pigments are characterized by the presence in the molecule of the methine group -C= or a conjugate chain of such groups. The first dyes of the polymethine type were prepared by Koenig in 1904 by rupture of the pyridine ring with cyanogen bromide in the presence of aromatic amines (Krahler, 1955):

Pyridine | Aromatic amine | Polymethine

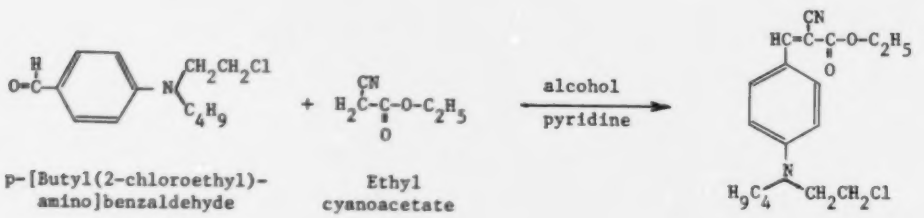
These products were of little commercial importance because of their lack of fastness to alkali. In 1925, Koenig patented a very similar dye that had the color intensity of his earlier compounds, but was also fast to alkali and acid. This dye was marketed as Astraphloxine FF and is today known as C.I. Basic Red 12 (C.I. 48070):



In the decade preceding World War II, I.G. Farben patented a color range of polymethine dyes of the Astraphloxine type, which were sold under the trade name Astrazone. The methine colors are of limited importance, though some of them have been patented primarily as yellow disperse dyes.

SYNTHESIS OF METHINES

No process chemistry descriptions were found for the methine dyes listed in Table 1. However, Krahler (1955) described a "typical methine dye synthesis" as the condensation of ethyl cyanoacetate and p-[butyl(2-chloroethyl)amino] benzaldehyde in the presence of an alcohol and pyridine to give a yellow dye known as Celliton Fast Yellow 7G:



p-[Butyl(2-chloroethyl)-amino]benzaldehyde

Ethyl cyanoacetate

Celliton Fast Yellow 7G

SYNTHESIS OF POLYMETHINES

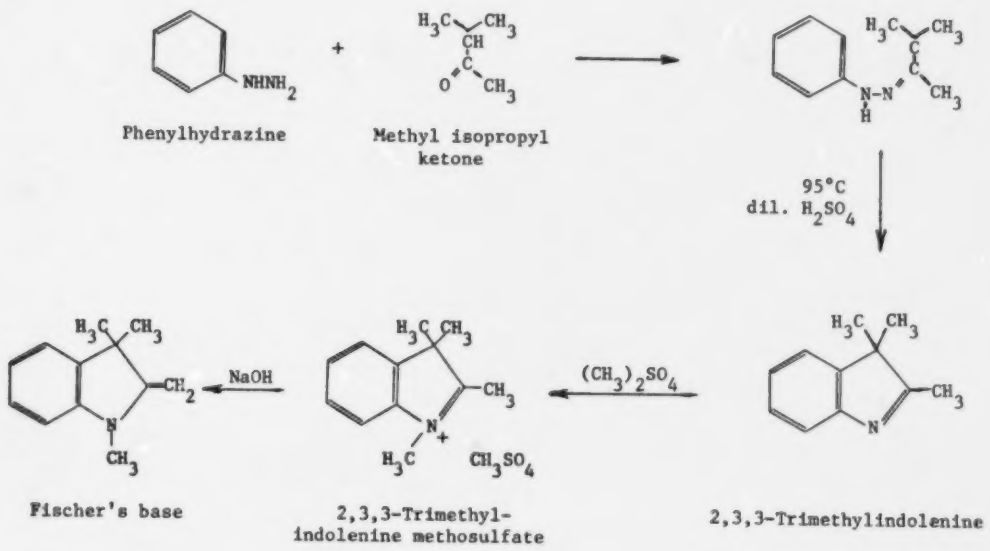
Two processes for the synthesis of the polymethines known as the Astrazones were found: Fischer's base synthesis and Fischer's aldehyde synthesis. Industry sources* indicated that many of the proprietary polymethine dyes (i.e., those for which no C.I. number or structural formula is given) used these process routes, but some dyes have a more unique process chemistry.

---

*Bochner, M. B., Technical Director, Atlantic Dyestuffs, Atlantic Chemical Corp., Personal communication, February 1982.
Stein, A., E.I. duPont de Nemours and Co., Inc., Personal communication, February 1982.

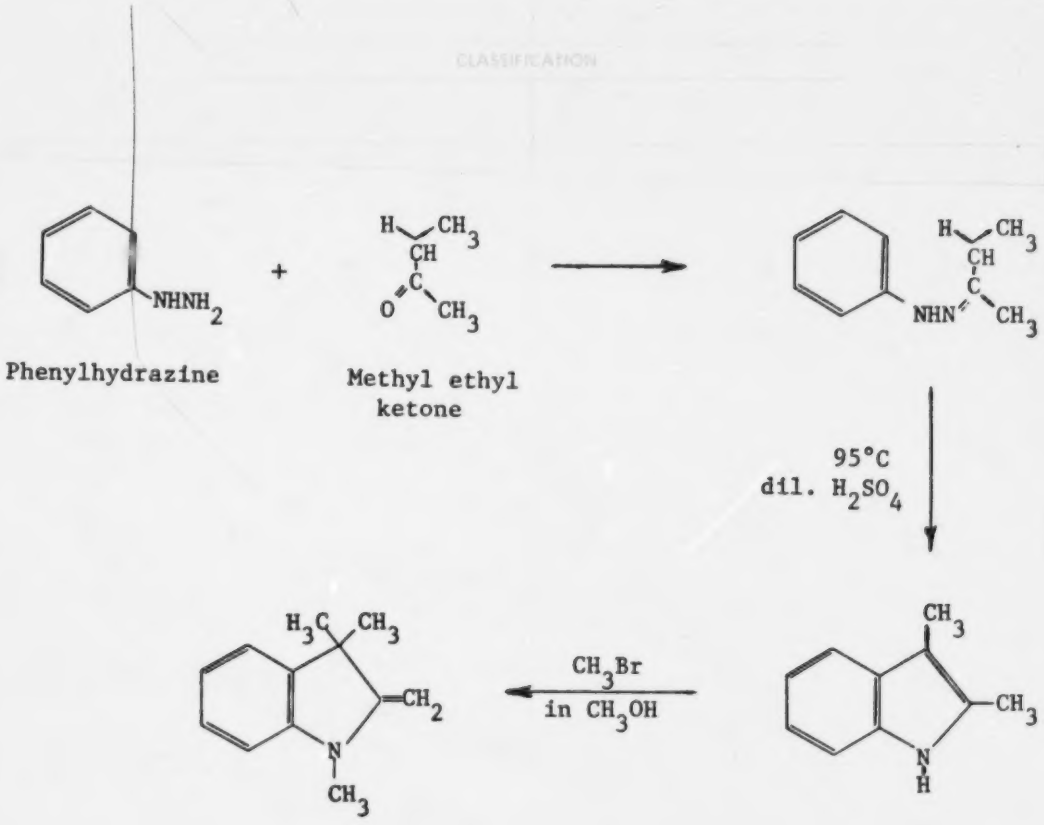
Synthesis of Fischer's Base

Abrahart (1977) describes the synthesis of Fischer's base from the condensation of phenylhydrazine with methyl isopropyl ketone, followed by methylation. This process is known as Fischer's indole synthesis.



According to Venkataraman (1952) and a BIOS report (BIOS, 1945), the methylation is performed with dimethyl sulfate.

Another version of Fischer's indole synthesis is also described in the BIOS report and by Venkataraman. This process involves the condensation of phenylhydrazine with methyl ethyl ketone (MEK) rather than using methyl isopropyl ketone. According to the BIOS report, the methylation is performed with bromomethane in methanol rather than the dimethyl sulfate used with isopropyl ketone:



Phenylhydrazine

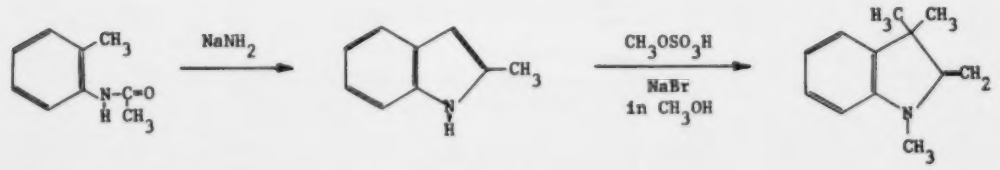
Methyl ethyl ketone

Fischer's base

2,3-Dimethylindole

MEK is roughly one-third the cost of methyl isopropyl ketone. However, the process route starting with methyl isopropyl ketone is usually preferred because of the more expensive capital costs associated with the MEK process, which must use a nickel autoclave because of the corrosive conditions of the process.

Fischer's base may also be prepared from acetyl-o-toluidine, which is reacted with sodamide to produce 2-methylindole (BIOS, 1945), which in turn is methylated with methylsulfuric acid and sodium bromide in methanol:

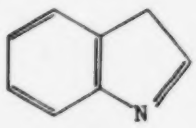


Acetyl-o-toluidine

2-Methylindole

Fischer's base

However, the Fischer's base obtained by this process always contains indolenine and must be after-methylated with dimethyl sulfate.



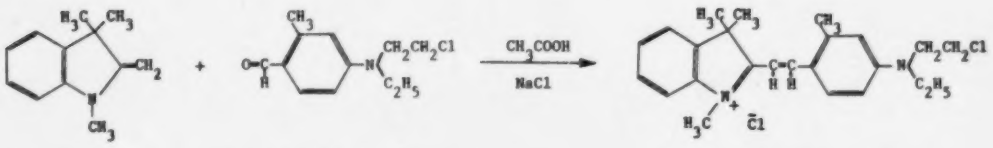
Indolenine

Methylation of the 2-methylindole is not as easy as the 2,3-dimethylindole in the process using MEK (BIOS, 1945). It is doubtful this process is of major commercial significance.

Fischer's Base Synthesis Route

This process involves the condensation of Fischer's base with an aromatic aldehyde in the presence of acetic acid.

The synthesis of C.I. Basic Violet 7 (C.I. 48020), also known as Astrazon Red 6B, is a typical example of this reaction. It is produced by condensing Fischer's base with 4-[(2-chlorethyl)ethylamino]-o-tolylaldehyde (BIOS , 1945) in glacial acetic acid:



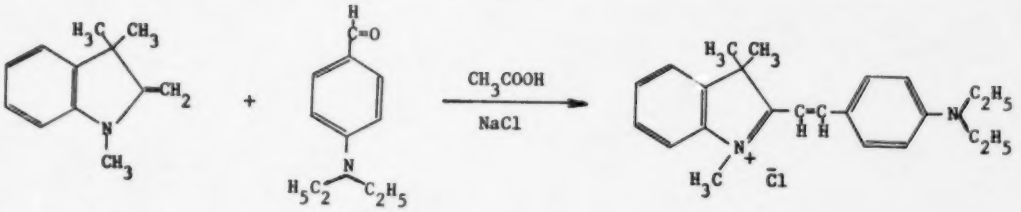
Fischer's base

4-[(2-Chloroethyl)ethylamino]-o-tolylaldehyde

C.I. Basic Violet 7
C.I. 48020

This reaction is reported to occur when the reactants are heated to 95 to 100°C for about 30 minutes. The solution of the dyestuff is then diluted with water and the dyestuff salted out with sodium chloride, followed by a recrystallization from water to increase the purity.

C.I. Basic Violet 16 (C.I. 48013), also known as Astrazon Red Violet 3R, is made by condensing Fischer's base with p-diethylaminobenzaldehyde (Krahler, 1955; Steadman et al., 1977):

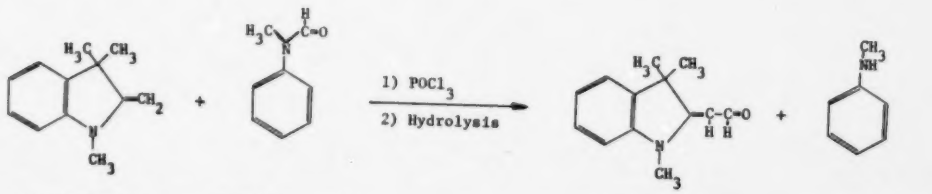


Fischer's base | p-Diethylamino-benzaldehyde | C.I. Basic Violet 16 C.I. 48013

Based on the recipe for C.I. Basic Violet 7 (BIOS, 1945), this reaction is probably conducted in glacial acetic acid. The resultant dye is salted out of the reaction mixture and filtered from the mother liquor. Recrystallization from water is used to obtain the dyestuff in a pure state.

Synthesis of Fischer's Aldehyde

Fischer's aldehyde is obtained by direct formylation of Fischer's base using N-methylformanilide and phosphorus oxychloride (or phosgene, according to Venkataraman, 1952) and hydrolyzing the product by adding dilute acid:



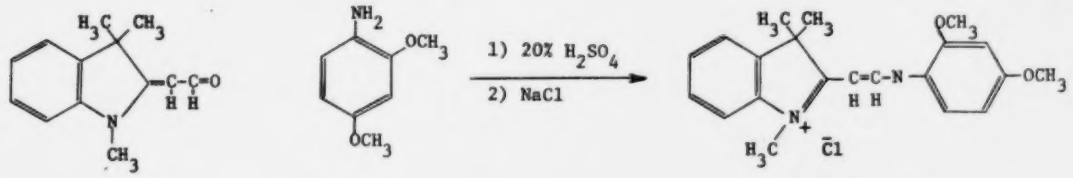
Fischer's base | N-Methylformanilide | Fischer's aldehyde | N-Methylaniline

BIOS (1954) reported the use of o-dichlorobenzene as the solvent for this reaction. After reaction, the o-dichlorobenzene, N-methylaniline, and unreacted Fischer's base are distilled with steam in the presence of alkali. The distillation residue is dried, and the nonvolatile Fischer's aldehyde recrystallized from ligroin.*

*A saturated volatile fraction of petroleum boiling in the range 20 to 135°C.

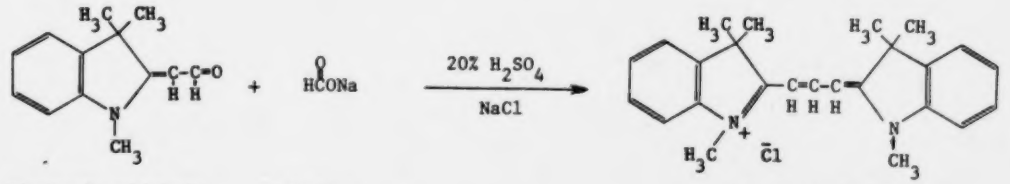
Fisher's Aldehyde Synthesis Route

This route synthesizes polymethine dyes using the condensation of Fischer's aldehyde (1,3,3-trimethyl-$\Delta^{2,\alpha}$-indolineacetaldehyde) with an aromatic amine in the presence of mineral acid. The synthesis of C.I. Basic Yellow 11 (C.I. 48055), also known as Astrazon Yellow 3G, is a typical example of this reaction. It is made by the following process (Krahler, 1955; BIOS, 1945):



Fischer's aldehyde — 2,4-Dimethoxyaniline — C.I. Basic Yellow 11 C.I. 48055

The crude dyestuff is isolated (probably filtered from the mother liquor) and recrystallized from water. Other dyes are made with hydrochloric acid instead of sulfuric acid. For these dyes the solvent system is water. Other Fischer's aldehyde syntheses may take place in organic solvents. The Colour Index (The Society of Dyers and Colourists, 1980) reported that the condensation of Fischer's aldehyde with sodium formate to make C.I. Basic Red 12 occurs in acetic anhydride in the presence of magnesium oxide. Venkataraman (1952) described yet another route to make C.I. Basic Red 12 in which Fischer's indole synthesis is used to produce the 2,3,3-trimethylindolenine intermediate, which is reacted with triethyl orthoformate (triethoxymethane) in a pyridine solution, followed by hydrolysis.



Fischer's aldehyde — Sodium formate — C.I. Basic Red 12 C.I. 48070

This procedure is similar to another procedure listed in the Colour Index that describes reacting 3-methylindole (skatole) with chloromethane and converting the base to the dye C.I. Basic Red 12 with trimethyl orthoformate (trimethoxymethane).

SECTION 4

ORGANIC INTERMEDIATES AND REAGENTS IN METHINE AND POLYMETHINE DYE PRODUCTION

A list of organic intermediates and reagents used to produce some of the polymethine and methine dyes in the United States was complied from information in the Colour Index (The Society of Dyers and Colourists, 1971), BIOS (1945), and Venkataraman (1952). Table 3 lists the organic intermediates, and Table 4 lists the organic reagents used in the production of the six dyes for which process information was available:

C.I. 48013	Basic Violet 16
C.I. 48020	Basic Violet 7
C.I. 48035	Basic Orange 21
C.I. 48055	Basic Yellow 11
C.I. 48070	Basic Red 12
C.I. 48100	Basic Yellow 23

The remaining 27 dyes and pigments are of unknown chemical structure and therefore no process information is available.

Tables 3 and 4 also identify those substances which, if present in solid residues, are subject to regulation as hazardous wastes under RCRA (Federal Register, 1980). These substances are identified by their hazard code.

Table 3

ORGANIC INTERMEDIATES USED TO PRODUCE METHINE AND POLYMETHINE DYES AND PIGMENTS

Intermediates	Hazardous Waste Listing[a]
Acetic anhydride	
Aniline, 2,4-dimethoxy-	
_____, N-methyl-	
Benzaldehyde, p-diethylamino-	
2-Butanone (Methyl ethyl ketone; MEK)	I, T
_____, 3-methyl- (Methyl isopropyl ketone)	
Dimethyl sulfate	T
Formanilide, N-methyl-	
Indole, 2,3-dimethyl-	
_____, 2-methyl-	
_____, 3-methyl- (Skatole)	
Indolenine	
_____, 2,3,3-trimethyl-	
_____, 1,3,3-trimethyl-2-methylene-	
$\Delta^{2,\alpha}$-Indolineacetaldehyde, 5-chloro-1,3,3-trimethyl-	
_____, 1,3,3-trimethyl-	
Methane, bromo-	T
____, chloro-	I, T
_____, trimethoxy- (Orthoformic acid trimethyl ester)	
Phenylhydrazine	
Sodium formate	
Toluidine, acetyl-o-	
_____, (2-hydroxyethyl)ethylamino-m-	
Tolyaldehyde, 4-[(2-chloroethyl)ethylamino]-o-	

[a] Hazard codes from the Federal Register indicate the basis for EPA listing the material hazardous: Ignitable (I) and Toxic (T)

Table 4

ORGANIC REAGENTS USED TO PRODUCE
METHINE AND POLYMETHINE DYES
AND PIGMENTS

Reagents	Hazardous Waste Listing[a]
Acetic acid, glacial	
Benzene, o-dichloro	T
Ligroin (Benzine)	
Methanol	T
Methylsulfuric acid	
Phosgene	T

[a]Hazard codes from the Federal Register (1980) indicate the basis for EPA listing the material hazardous: ignitable (I) and toxic (T).

SECTION 5

SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING

The wide range of dye and pigment production processes and the specific plant characteristics and process control capabilities make estimation of material losses during dye manufacture a difficult task. In general, the most significant material losses are intermediates that do not react and by-products, such as incomplete dye or pigment molecules. The intermediates and by-products from dye manufacturing are present either in the product or in the solid residue streams regulated under RCRA--wastewater, solid residues, or the vapor and dust emissions. The material in the wastewater is discharged in the plant effluent (although some is destroyed by treatment as described below), and some is discharged on wastewater treatment solids.

OVERVIEW OF DYE AND PIGMENT PRODUCTION PROCESSES

Figure 1 illustrates the dye and pigment manufacturing process and shows where the losses of materials occur. The dye manufacturing equipment required to produce methine and polymethine dyes and pigments consists of well-stirred tanks, autoclaves, plate and frame filter presses, tunnels dryers or vacuum tray dryers, grinders, and blenders.

The dye or pigments are produced in batches, and the plants typically contain several reactor trains. Complex dyes and pigments may require use of several reactor trains. Production of colors is usually rotated by set schedules from light- to dark-colored dyes to minimize the impact of dye carry-over from multiple use of the equipment.

Most of the methine and polymethine dyes and pigments are produced in a single process step by condensing the organic constituents selected, as described in Section 3. All the dyes are precipitated out of the reaction mixture [usually by the addition of salt (salting out)] and filtered from the mother liquor (Steadman et al., 1977). Often the dye is obtained in a higher purity by recrystallization from water (BIOS, 1945). Pigments are insoluble and do not require salting out. The resulting slurry of a pigment or purified dye is filtered using a filter press, and air is blown through the press cake to remove as much mother liquor as possible (Kent, 1974). The cake is removed from the press and dried in an atmospheric tunnel dryer or a vacuum tray dryer. The dye is then ground in a swing hammer mill and thoroughly mixed in a blender.

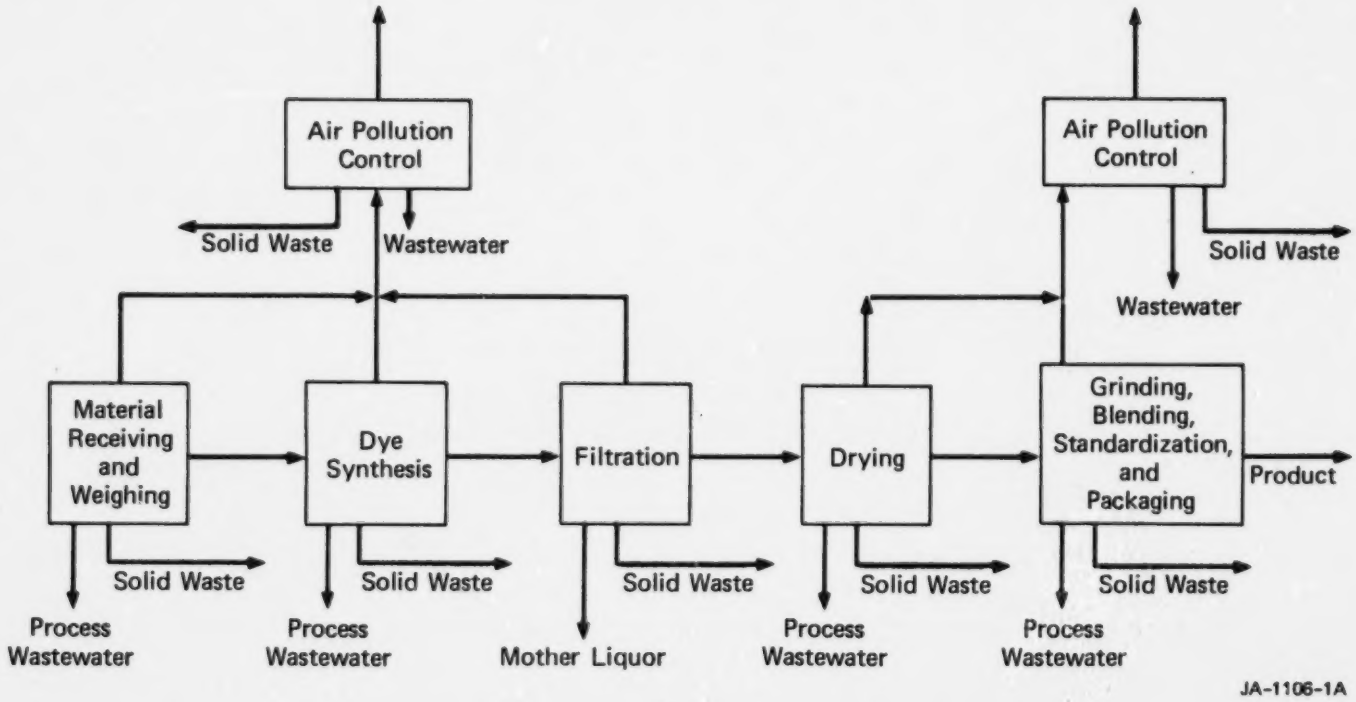


FIGURE 1 PRODUCTION OPERATIONS THAT ARE SOURCES OF WASTE EMISSIONS IN DYE AND PIGMENT MANUFACTURE

The dye concentrations of the polymethine Astrazones ranged from 27% to 45% by weight (BIOS, 1945). Often sodium chloride or Glauber's salt (sodium sulfate) is added to the blender to reduce the dye concentration to a standard strength. The amount of salt added to a dye depends on the dye and the producer and may even vary among dye batches at a single facility. However, because the polymethine dyes are acid-soluble, there would be water solubility problems with the product if only salt were added for standardization. Some manufacturers use solid acids, such as boric acid, to aid in solubility. Yellow dextrin is also added by some as a blending agent. The diluent will usually contain wetting agents and emulsifiers and dedusters, usually hydrocarbon oils, to improve the dyestuff properties.

SOURCES OF WASTES

The sources of wastes from dye manufacture identified in Figure 1 are summarized below by source:

Materials Handling - Air emissions from raw material dusting and volatilization, solid residues on shipping containers, and process wastewaters from equipment wash down.

Dye Synthesis - Air emissions from the volatilization of intermediates in reaction vessels, solid residues from spills, and process wastewater from equipment washdown.

Product Filtration - Air emissions from the volatilization of unreacted intermediates during material handling, solid residues from spills, and process wastewater from equipment washdown. A significant additional source of process wastewater is the mother liquor.

Drying - Air emissions from volatilization of by-products and unreacted intermediates in the drying oven and solid residues from spills and dusting of the product dye.

Grinding, Blending, Standardization, and Packaging - Solid residues from dusts produced by the grinding operations that may be in the air streams from vent systems designed to keep the material out of the workplace environment or in the solid residues from spills.

Air Pollution Control - Solid Residues from baghouses or scrubbers collecting fine dusts and process wastewater from scrubbers.

Previous studies (Lapp et al., 1979; Bomberger and Boughton, 1983) have demonstrated that the major potential source of emissions is the process wastewater, principally because it contains the mother liquor. Based on the chemistry discussed in Section 3, the mother liquors will probably contain unreacted intermediates, reaction by-products, unprecipitated dye or pigment, and salt. They may also contain mineral acids, such as sulfuric and hydrochloric acid, or organic acids, such as acetic acid. Pyridine, which is used a a solvent in at least one dye synthesis and various alcohols, may also be present.

Keinath and Pollack (1978) analyzed two different batches of an aqueous mother liquor from the production of the polymethine dye C.I. Basic Yellow 28 (C.I. 48054). The results in ppm are shown below:

	Batch A	Batch B
Chloride	58,565	60,315
Suspended solids	7.6	62
Dissolved solids	118,111	117,500
Total solids	117,263	115,710
Volatile suspended solids*	9.1	4,498
Biological oxygen demand (BOD)	--	4,700
Total Kjeldahl nitrogen	--	86.1
Alkalinity	43.6	60.2

Wastewater treatment, which can convert some of the aqueous material to a solid residue is discussed separately below.

Solid residues on discarded shipping containers are also an important potential source of emissions.

If Fisher's aldehyde is synthesized at the dye manufacturing site, instead of being purchased, a mixture of o-dichlorobenzene, N-methylaniline, and Fisher's base and water is produced when the reaction mixture is distilled to purify the aldehyde. A ligroin stream is also produced that is contaminated with these compounds and the aldehyde as well. If the organics are reclaimed in solvent stills, hazardous still bottoms may be produced; however, if the organics are not reclaimed but are disposed of, they might constitute hazardous wastes.

WASTEWATER TREATMENT

Each dye producer may have a different wastewater treatment system. Some process wastewaters are discharged directly to sewers and thus to publicly owned treatment works. Some wastewaters are sealed in drums, which are placed in a landfill. Some producers have on-site wastewater treatment plants. All these treatment plants will be site-specific designs with site-specific behavior. Several examples of on-site treatment facilities at dye production sites are discussed below to indicate the type of treatment often used and its effectiveness.

*Volatile suspended solids are generally organic material.

Anliker and Clarke (1979) reported an effluent concentration before treatment from a dyestuff manufacturer as 900 to 4000 ppm biological oxygen demand (BOD) and 600 to 1000 ppm total organic carbon (TOC). Other documents (such as EPA, 1975) give wastewater flows at six different dye manufacturing plants as 33, 114, 175, 200, 800, and 1800 liters/kg finished product. Sampling of these waste streams gave the following ranges: 200 to 5000 ppm BOD, 1200 to 4000 ppm chemical oxygen demand (COD), and 500 to 2000 ppm TOC.

Several studies have dealt specifically with the effect of common wastewater treatment processes on dye production wastewaters. Keinath and Pollack (1978) studied coagulation and flocculation using lime or ferric salts on wastewaters and found that only low organic removals (<40%) could be achieved. This probably reflects the fact that most dyes and their intermediates are water-soluble. Games and Hites (1977) described a wastewater treatment system at a facility that manufactures polymethine dyes and pigments. It consisted of neutralization in an equalization pond (raw effluent was acidic), aeration in two lagoons (in series) that were mechanically stirred to accelerate aerobic biological degradation, and settling in two large ponds (containing 80% of the total system volume). The dye manufacturing facility processed an average of 11.4 million liters per day of wastewater. Total residence time (by volume) in the treatment system averaged 19 days, but sometimes because of flow patterns the residence time was reduced to 6 days. The waste before treatment had a COD of about 670 ppm. Treatment plant performance averaged about 70% and 85% reduction of COD and BOD, respectively, to produce an effluent with a COD of 200 mg/liter and a BOD of 60 mg/liter. It was estimated that the daily discharge of organics in the treated water was 2200 kg.

Games and Hites (1977) identified and "semiquantified" the dichloromethane extractable compounds in the dye plant raw wastewater and final effluent. Their study consisted of composite sampling over a 2.5-month period. Their results, which showed wide concentration variations between different composites, indicated that grab sampling techniques would have been misleading. Table 5 shows some of the compounds believed to be from methine and polymethine dye production and the concentration range at which they were detected. The structures of these compounds are shown in Figure 2.

Games and Hites (1977) report the weekly composite concentration of the raw and final effluent for a few compounds to illustrate the deceptiveness of overall COD and BOD data. The results for three of the compounds reported in Table 5 are shown in Table 6. The concentration reduction due to treatment should be compared with values of about 70% for COD reduction and 85% for BOD reduction. The variation in residence time (6 to 19 days) probably accounts for some of the variation observed in these data. The concentration of 1,3,3-trimethyl-$\Delta^{2,\alpha}$- indolineacetaldehyde appears to decrease to about the same extent as one would expect from the COD data. However, the 1,3,3-trimethoxindole concentration actually increased after passing through the treatment plant. Games and Hites believe that the 2-methylindoline data are inconclusive.

Table 5

PARTIAL LIST OF COMPOUNDS FOUND BY GAMES AND HITES (1977)
IN THE COMPOSITE SAMPLES COLLECTED FROM A DYE MANUFACTURING PLANT

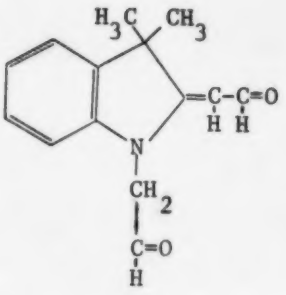
Compound	Raw Wastewater Concentration[b,c] (ppb)	Final Effluent Concentration[c] (ppb)
3,3-Dimethyl-1,$\Delta^{2,\alpha}$-indolineacetaldehyde[a]	ND	9-460 (4)
2-Methylindoline[a]	26-400 (4)	28-610 (6)
Trimethylindole (isomer unspecified)	ND	13-72 (7)
1,3,3-Trimethyl-$\Delta^{2,\alpha}$-indolineacetaldehyde[a]	3-52 (6)	14-440 (7)
1,3,3-Trimethyl-2-methyleneindoline[a]	320 (1)	13-130 (7)
1,3,3-Trimethyloxindole[a]	65-510 (8)	10-3600 (9)
1,3,3-Trimethyloxindole + C_2H_4[d]	ND	27-78 (7)

[a] Refers to compounds whose structures are shown in Figure 2.

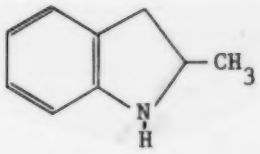
[b] ND means "not detected."

[c] Number in parentheses refers to the total number of composites in which the compound was found. The raw effluent is based on eight total samples and the final effluent on nine total samples.

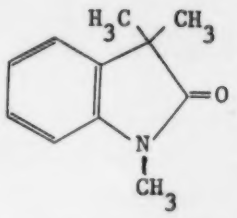
[d] This compound has a similar mass spectrum to 1,3,3-trimethyloxindole, and the high resolution mass spectrometry indicated that it has two additional CH_2 units.



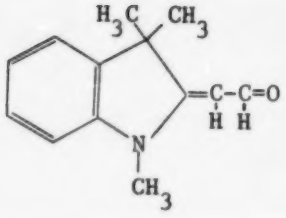
3,3-Dimethyl-1,$\Delta^{2,\alpha}$-indolineacetaldehyde



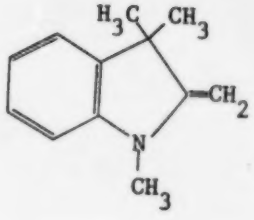
2-Methylindoline



1,3,3-Trimethyloxindole



Fischer's aldehyde



Fischer's base

FIGURE 2 STRUCTURES FOR SOME OF THE COMPOUNDS FOUND BY GAMES AND HITES (1977) IN THE DYE MANUFACTURING FACILITY WASTEWATER

Table 6

CONCENTRATIONS OF VARIOUS INDIVIDUAL COMPOUNDS FOUND BY GAMES AND HITES (1977) IN THE COMPOSITE SAMPLES COLLECTED FROM A DYE MANUFACTURING PLANT (ppb)[a]

Date Collected	2-Methylindoline		1,3,3-Trimethyloxindole		1,3,3-Trimethyl-$\Delta^{2,\alpha}$-Indolineacetaldehyde	
	Raw Wastewater	Final Effluent	Raw Wastewater	Final Effluent	Raw Wastewater	Final Effluent
3/22-3/26	49	--[b]	160	--[b]	27	--[b]
2/24-4/3	--[c]	ND	--[c]	340	--[c]	57
4/5-4/9	Lost	52	Lost	300	Lost	440
4/19-4/23	ND	140	320	480	36	14
4/26-4/30	400	82	510	680	52	14
5/3-5/7	26	610	160	3600	ND	33
5/10-5/14	ND	56	110	660	ND	55
5/17-5/21	ND	28	310	740	20	16
5/24-5/28	99	ND	130	150	18	ND
6/1-6/4	ND	ND	65	100	3	ND

[a] ND means "none detected."

[b] 3/22 to 3/26, only raw composite collected.

[c] 3/24 to 4/3, only final composite collected.

Ruling out synthesis of the oxindole in the treatment system, Games and Hites concluded that chemical or biological degradation of dye molecules was causing the increase in concentration. The reactions that are apparently occurring are summarized in Figure 3. Oxidative decomposition of Astraphloxine FF (C.I. Basic Red 12, C.I. 48070) or similar dyes could have led to the formation of the oxindole in the wastewater treatment plant. In addition, autoxidation of Fischer's base may have formed the oxindole during wastewater treatment as well as during in-plant processing. Games and Hites pointed out that Fischer's base was found in only one of the raw effluent samples but was in seven of the final effluent composites (see Table 5), indicating that Fischer's base was also being formed in the treatment plant. This suggested dye decomposition followed by autoxidation was the cause of the oxindole concentration increase.

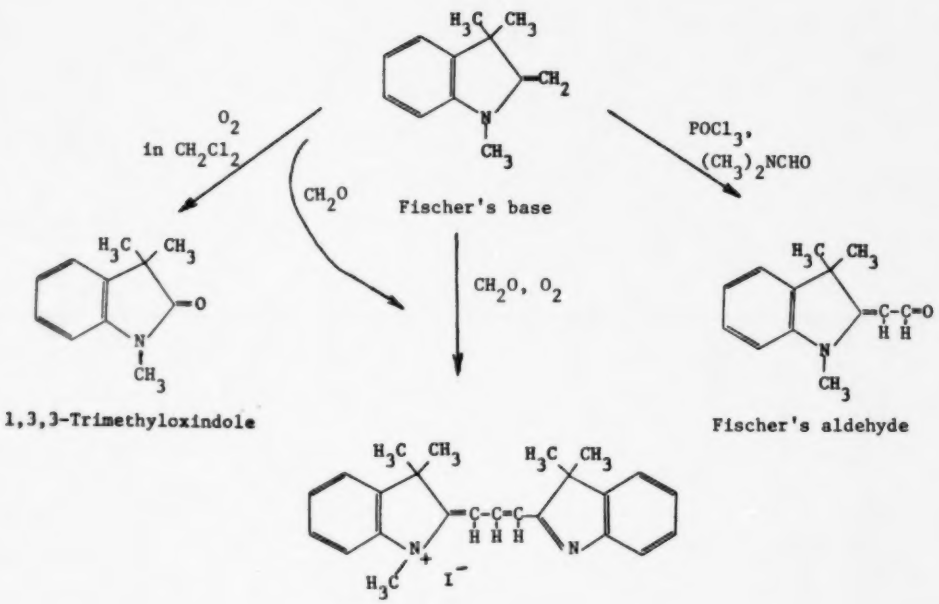


FIGURE 3 SUMMARY OF REACTIONS INVOLVING 1,3,3-TRIMETHYL-2-METHYLENEINDOLE

SECTION 6

MATERIAL IN THE WASTE STREAMS FROM METHINE AND POLYMETHINE DYE AND PIGMENT PRODUCTION

An in-depth discussion of the waste emissions from the methine and polymethine dye and pigment industry is impossible when restricted to public sources of information. There are 25 dyes and pigments of the 33 commercially signficant dyes and pigments (by U.S. production) listed in Table 1 for which there are no Colour Index number, no structure reported and no process description given. An additional two dyes have been assigned a C.I. number, but no process information is available. Therefore, for 27 methine and polymethine dyes and pigments, no information is available about intermediates and other materials of production. Five of these 27 dyes are included in the 8 dyes and pigments of known 1979 U.S. commercial production volume as listed in Table 2. A quantitative estimate of the intermediates and by-products in the solid residues and aqueous waste streams from manufacturing was not attempted because we did not have access to the required proprietary information.

Table 7 lists the polymethine dyes for which process chemistry was available and the amount of each produced. (No information was found on methine dye process chemistry.) The table also identifies the known intermediates and other organic chemicals used in the production of the dyes. Table 7 does not identify or quantify process chemistry by-products that are likely to be present, for example, isomers of required intermediates and the reaction products of these with the other intermediates and reagents used in the process. The by-products were not included in this study because very little useful information dealing with the amount or nature of these by-products was found.

Table 8 gives the full names of the producers associated with the letter codes used in Table 7. Table 9 lists all the producers of methine and polymethine dyes and lists the dyes they manufacture. The identity and corporate ownership of the producers is based on 1979 information. Since then, several dye production facilities or dye lines were sold. Sales that were announced in trade journals are shown as footnotes to Tables 8 and 9. A systematic search was not made to verify that all such sales have been listed, so the tables may not be complete.

Table 7

ORGANICS THAT MAY APPEAR IN THE WASTE STREAMS FROM THE PRODUCTION OF SOME OF THE POLYMETHINE DYES

1979 U.S. Commercial Producers[a]	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment[b]
ATL BAS DUP TRC VPC	48013	Basic Violet 16	120	Basic Violet 16 p-Diethylamino benzaldehyde Glacial acetic acid 1,3,3-Trimethyl-2-methyleneindole
ATL	48020	Basic Violet 7	>2	Basic Violet 7 4-[(2-Chloroethyl]ethylamino]-o-tolylaldehyde Glacial acetic acid 1,3,3-Trimethyl-2-methyleneindole
ATL DUP TRC	48035	Basic Orange 21	227	Basic Orange 21 2-Methylindole 1,3,3,-Trimethyl-$\Delta^{2,\alpha}$-indolienacetaldehyde
BAS VPC	48054	Basic Yellow 28	>5	Basic Yellow 28 Unknown
ATL DUP	48055	Basic Yellow 11	249	Basic Yellow 11 2,4-Dimethoxyaniline 1,3,3-Trimethyl-$\Delta^{2,\alpha}$-indolineacetaldehyde
ACY DUP VPC	48070	Basic Red 12	>7	Basic Red 12 Acetic anhydride Methyl chloride 3-Methylindole Methyl orthoformate Sodium formate 1,3,3-Trimethyl-$\Delta^{2,\alpha}$-indolineacetaldehyde
BAS	48100	Basic Yellow 23	>2	Basic Yellow 23 5-Chloro-1,3,3-trimethyl-$\Delta^{2,\alpha}$-indolineacetaldehyde 1,2,3,4-Tetrahydrocarbazole
EKT	48420	Disperse Yellow 99	>2	Disperse Yellow 99 Unknown

[a] The letter codes are defined in table 8.

[b] By-products should be included for each dye.

Table 8

DIRECTORY OF DYE AND ORGANIC PIGMENT MANUFACTURERS, 1979

Names of manufacturers that reported production and/or sales of methine and polymethine dyes and pigments to the U.S. International Trade Commission for 1979 are listed below in order of their identification codes as used in Table 7.

Code	Name of Company
Dye Manufacturers	
AC	American Color & Chemical Corp.
ACY	American Cyanamid Co.
ATL	Atlantic Chemical Corp.
BAS	BASF Wyandotte Corp.
DUP[a]	E. I. duPont de Nemours & Co., Inc.
EKT	Eastman Kodak Co., Tennessee Eastman Co. Div.
SDC	Martin-Marietta Corp., Sodyeco Div.
TRC	Toms River Chemical Corp.
VPC	Mobay Chemical Corp., Verona Dyestuffs Div.
Pigment Manufacturers	
CGY	Ciba-Geigy Corp.
HRC	Harmon Colors Corp.

[a] In 1979 duPont sold its paper dye operations to Mobay Chemical Corp., and its textile dye operations to Ciba-Geigy Corp. and Crompton and Knowles Corp.

Table 9

1979 PRODUCERS OF METHINE AND
POLYMETHINE DYES AND PIGMENTS

C.I. No.	C.I. Name
American Color & Chemical Corp.	
--	Disperse Yellow 118
American Cyanmid Co.	
48070	Basic Red 12
--	Basic Red 14
--	Basic Yellow 78
Atlantic Chemical Corp.	
48013	Basic Violet 16
48020	Basic Violet 7
48035	Basic Orange 21
48055	Basic Yellow 11
--	Basic Red 14
--	Basic Red 15
--	Basic Yellow 13
--	Basic Yellow 29
BASF Wyandotte Corp.	
48013	Basic Violet 16
48054	Basic Yellow 28
48100	Basic Yellow 23
--	Basic Red 14
--	Basic Red 15
--	Basic Red 49
--	Basic Yellow 29
--	Basic Yellow 49
--	Basic Yellow 64
--	Basic Yellow 65
Ciba Geigy Corp.	
--	Pigment Yellow 129
E. I. duPont de Nemours & Co., Inc.[a]	
48013	Basic Violet 16
48035	Basic Orange 21
48055	Basic Yellow 11
48070	Basic Red 12
--	Basic Red 14
--	Basic Red 15
--	Basic Red 49
--	Basic Violet 15
--	Basic Yellow 13
--	Basic Yellow 29
--	Basic Yellow 53
--	Basic Yellow 58
--	Basic Yellow 79
--	Disperse Yellow 131
Eastman Kodak Co., Tennessee Eastman Co. Div.	
48420	Disperse Yellow 99
--	Disperse Yellow 88
--	Disperse Yellow 200
Harmon Colors Corp.	
--	Pigment Yellow 139
Martin-Marietta Corp., Sodyeco Div.	
--	Disperse Yellow 125
--	Disperse Yellow 207
--	Disperse Yellow 208

Table 9 (Concluded)

C.I. No.	C.I. Name
Toms River Chemical Corp.	
48013	Basic Violet 16
48035	Basic Orange 21
48055	Basic Yellow 11
--	Basic Red 49
Mobay Chemical Corp., Verona Dyestuffs Div.	
48013	Basic Violet 16
48035	Basic Orange 21
48054	Basic Yellow 28
48055	Basic Yellow 11
48070	Basic Red 12
--	Basic Blue 69
--	Basic Red 14
--	Basic Red 49
--	Basic Yellow 13
--	Basic Yellow 21
--	Basic Yellow 29
--	Disperse Yellow 93

[a] In 1979 duPont sold its paper dye operations to Mobay Chemical Corp., and its textile dye operations to Ciba-Geigy Corp. and Crompton and Knowles Corp.

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